

Benefits from coking of heavy feedstocks

Research into the thermal processing of heavy oil using advanced analytical and laboratory techniques has revealed that huge gains are possible, thanks to a new reactor configuration based on the marriage of two commercial technologies

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Limits in the ability of existing refinery infrastructure to process the most highly condensed, heavy material contained in a barrel of crude oil have emerged as a significant impediment in meeting world energy demands. While the supply of oil is often identified as the bottleneck in the refining chain, it is currently only light sweet crude that is in short supply. Although the shortfall in this conventional refining feedstock can be addressed through an increase in the supply of heavier sour crudes, the existing refining infrastructure designed to process these heavy barrels is already overwhelmed. Recent trends in the price of heavy sour crude relative to the light conventional benchmark support this notion.

Moving forward, the oil industry has recognised that the global reliance on heavy oil feedstocks will only increase, and that significant investment in new refinery capacity is required to accommodate this shift. It is projected that by 2010 almost 85% of the oil processed in Canada, the biggest supplier of crude oil and petroleum products to the US, will be of the heavy variety. As evidence, the oil sands of Northern Alberta are being developed at a rapid pace, with production projected to reach 3MMBPD by 2030. Investment is required in those units whose function it is to elevate the quality of heavy oil to a level where it can be accepted by existing refining infrastructure: a process often referred to as primary upgrading. Without a parallel ramping-up of primary upgrading capacity, these new barrels of heavy oil will have little value, since no refinery will have the capacity to process them.

The main function of any primary upgrading process is to convert the heavy feed into a product with increased hydrogen and reduced heteroatom content. The choice of an upgrading technology is dependent upon the prevailing micro and macro economic conditions. Technology selection is

influenced by such factors as the cost of energy used by the process, local labour costs, the value of the products of the process, the price of the heavy feedstock and the value of any by-product streams. When considering integration of the upgrading process, it is also important to take into account the form of energy that is generated by the process, as this will dictate where it can be used.

Original residua processing methods

The original methods for processing heavy residua were based on exposing the hydrocarbon feedstocks to reduced thermal environments. The endothermic cracking reactions associated with these operating conditions produce free radicals, initiating a sequence of events referred to as coking. In the coking process, the hydrogen contained in the feed is essentially reshuffled between the coke, gas and liquid products of the reaction. The original cokers focused on the production of solid coke as the primary saleable product. Later, semi-batch processes were developed, with an emphasis on the production of hydrocarbon mixtures with an atmospheric boiling range of less than 524°C. In these units, coke production is delayed, occurring in the downstream coke drum and not in the tubes of the heater where the energy required to drive the endothermic reactions is added. The adiabatic nature of the coke drum essentially limits the conversion in these processes.

The Fluid Coking process, commercialised by Exxon in the 1950s, circumvents this problem by carrying out the thermal reactions on a fluidised bed of hot solids. In this case, the feed liquid and energy streams are decoupled and introduced separately into the reactor. While a yield advantage has been attributed to this configuration, experience has shown that it is realised at the expense of product oil quality. Although other options exist, delayed coking together with the proprietary

Fluid and ExxonMobil Flexicoking are the dominant commercial processes for upgrading the heaviest fraction of crude oil into distillable liquids.

Fluid and delayed coking are classified as mature technologies, located on the flat part of the development "S" curve. But while these technologies are considered mature, our fundamental knowledge of coking chemistry is not. Through the advent and application of novel experimental and measuring techniques, data have become available that make the realisation of a step change in coker performance apparent. In fact, a recent study of upgrading technologies has placed coking technologies based on this new research on the steep part of the "S" curve, indicating the potential for significant gains.

So where are these gains to be had and how can they be achieved? To answer this question it is convenient to summarise the basic elements that all coking processes must have:

- Coking processes are endothermic, requiring heat input
- At increased reaction extents the heavy liquid feed is converted into two phases: a solid coke phase and a gas phase. A fraction of the gas is made up of molecules that are distillable, while the balance will remain as a gas at ambient conditions. The distillable liquids are referred to as liquid products
- While at reactor conditions, the liquid products can be converted thermally to lighter fractions, including non-condensable gases. The incremental gas generated by this process effectively steals hydrogen from the distillable liquid fraction that can ill-afford to lose it. Significant downstream capital and operating cost are required to replace and supplement lost hydrogen.

Recent work suggests that both physical and chemical processes are important in coking and points to the following simplified picture describing the residua conversion process (Figure 1):

- Under thermal conditions above

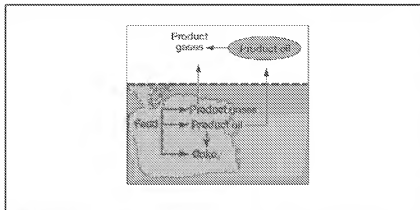


Figure 1 Simplified model describing the thermal coking process. The horizontal dashed line represents the gas-liquid interface existing in the reactor, where the shaded area represents the liquid phase. Solid arrows represent chemical conversion processes, while open arrows pertain to physical transfer between phases

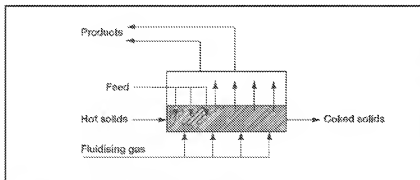


Figure 2 Schematic of the cross-flow coking (ETX) concept

approximately 400°C, the heavy residuum molecules in the feed react thermally in the liquid phase to form the desired liquid products. These species are present below their bubble point and hence have a tendency to move into the vapour phase

— Competing with this process are recombination reactions that increase the molecular weights of the reacting species and reduce the driving force for transport into the vapour phase. Species participating in this process are eventually lost to coke

— Liquid product that does manage to make it into the vapour phase will continue to crack, losing hydrogen to less valuable gases, until removed from the high severity environment present in the reactor.

From this simple model, it is apparent that to achieve the maximum benefit from the coking reactions the amount of time the liquid products remain in the liquid phase should be minimised, and the residence time of the gaseous products in the reactor should be as short as possible too.

To minimise the residence time of the liquid products in the reacting liquid phase it is important to keep the path length for their transfer into the gas

phase as short as possible. Fluid bed technology provides an attractive alternative in this regard due to the significant surface area available for distribution of the liquid reactant. The heat requirements of the reaction are met by the energy contained in the hot fluidised solids. Although these attributes are desirable, fluid bed technology introduces a significant constraint into the reactor design. Since the reacting liquid is carried on the fluidised solids, the residence times of the liquid feed and the fluidised solids are identical. The required residence time of the solids in the reactor is therefore determined by the time required for the feed to react completely. This time is 30–120 seconds, depending on the operating temperature of the reactor. In contrast, the optimal residence time of the liquid products, liberated as gases in the reactor, should be kept as short as possible. Since these two targets differ by an order of magnitude, it is essential that the fluxes of the two phases be decoupled as much as possible to allow for relatively independent optimisation.

Optimising residence times

The answer to the problem of how to accommodate the optimal residence

times of the solid and vapour phases is found in a commercial process, commonly applied in the drying industry, termed cross-flow fluidisation. In a cross-flow fluid bed, the solids flow perpendicular to the fluidising medium, affording essentially independent control of the flow behaviour of each phase. This is a key feature of the Envision Technologies ETX coker design (Figure 2).

In the ETX design, the fluidised bed of hot solids flows horizontally through the reactor: fluidising gas is introduced into the bottom of the reactor, perpendicular to the bulk flow of solids. The heavy oil feed is sprayed onto the hot fluidised solids introduced at one end of the unit. The reactions take place along the length of the reactor—evolving product into the gas phase. A slide gate producing the desired flux through the reactor controls the flow rate of the solids.

The benefits of the ETX design are a result of the combined characteristics of the solids and gas phase residence times. Due to the difficulties performing mixing studies at processing temperatures, the mixing characteristics of the solids and gas were studied at ambient conditions with a fluidised bed scaled down using the concept of dynamic similitude. A modified Froude number and a dimensionless fluidisation velocity were used for this purpose, as supported by literature on the subject. The bed was constructed to a dimension approaching commercial scale, with a footprint of 1m² and a height approaching 3m. Using solid tracers, the dependence of axial dispersion on fluidisation velocity was established. Under all conditions, the flow of solids approximated plug flow behaviour over a range of fluidisation velocities.

The dynamics of the gas phase in a fluidised bed are extremely complicated. To describe them, a mathematical model was developed using accepted concepts from supporting literature. The model was validated against gas tracer studies performed in the experimental fluidised bed. With this information, the residence time of the gas could be correlated to bed height and fluidisation velocity.

Direct operational and economic benefits are derived from the residence time distributions associated with both the solid and gas phases. As an example, consider the impact of the solids residence time distribution on reactor capacity. The reactor must provide sufficient solids residence time to allow the liquid feed coating the particles to react to completion. From basic reactor design theory, the minimum size reactor is realised when the residence time distribution of the reacting phase is plug

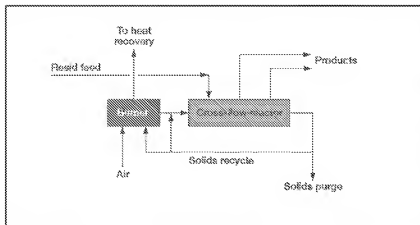


Figure 3 Basic flow diagram incorporating the cross-flow coking reactor

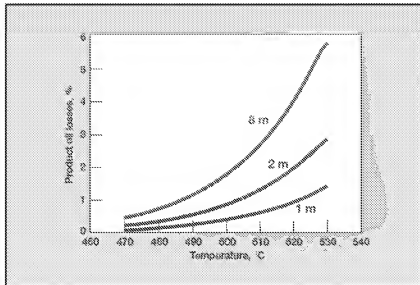


Figure 4 Impact of temperature on chemical changes occurring in the liquid phase, as a function of bed height, for a superficial gas velocity of 0.5 m/s. Reaction kinetics are based on the data of Levey et al (Fuel 66:358, 1987)

flow. As a result, a high reactor throughput can be realised in a cross-flow fluidised bed, because the solid phase, which carries the reactant, approaches plug flow. For instance, targeting a maximum of 0.5% losses of unreacted feed, the ETX reactor can accommodate 20 times the throughput per volume compared to the commercial fluid coking reactor, since the latter has a solids residence time distribution that is well mixed.

As a direct consequence of the cross-flow design, the bed height is relatively shallow at 1–2 m. This short path length limits the residence time of the gas phase, minimising gas phase severity and losses to over-cracking. Concurrent with increased liquid yields, the product quality is also improved as a result of reduced gas phase reactions — a significant advantage in an economic climate where hydrogen is an expensive commodity.

The nature of the ETX reactor also allows for some discrimination of products as they are evolved: products generated at the front end of the reactor will exit first, and it may be desirable to keep them separate from those products produced later on. For instance, depending upon the feedstock, the fraction recovered at the front of the reactor will be of adequate quality to be introduced directly into an FCC unit, bypassing a secondary upgrading step. For other feeds, such as residua from Athabasca bitumen, the quality of the feedstock is such that all products will probably require additional processing.

Operationally, the cross-flow unit introduces additional levers not available in traditional fluid coking. When liquid is sprayed onto a bed of solids, each liquid droplet is distributed among a fraction of the bed. If the flux of solid particles is inadequate for the flow rate of feed then agglomeration of

the bed particles can occur. In the extreme case, this can lead to defluidisation of the bed, which is a concern of all upgrading processes using fluidised beds. In order to ensure safe operation, a safety margin against defluidisation is maintained by adjusting the ratio of the liquid feed rate to the solids flux. At lower operating temperatures, since reaction times are longer and the liquid is more viscous, this ratio is kept lower, effectively spreading the feed out over more solids. Since the cross-flow design represents such a large capacity advantage over commercial fluid coking, the reactor can be made larger to accommodate higher solids throughputs while still maintaining a significant throughput advantage. As a result, cross-flow fluid beds are inherently better at managing defluidisation concerns, allowing the unit to be run more aggressively.

Due to the competing physical and chemical processes that occur in coking, there is a significant gain to be made by reducing the operating temperature in the reactor. Liquid yield increases of 6% by volume have been associated with a 35°C drop in temperature for a fluid bed reactor processing 1 MBPD. Other commercial operations have had similar experiences, with additional environmental benefits realised in the associated burner required to heat up the solids. The penalty to be paid comes in the form of an increased risk of defluidisation as a result of the reduction in temperature. However, because of the optimal solids residence time, the ETX design is able to operate at lower temperatures without increased risk in defluidisation, due to the additional operational levers introduced as a result of decoupling the gas and solids throughputs.

Cross-flow design benefits

The optimised design case for the ETX upgrading unit consists of integrated modules each processing 10 MBPD (Figure 3). Each reactor is 6 m in length, with a bed height of 2 m and an equivalent width. This reactor size includes allowances for feed distribution and solids withdrawal. The solids consist of either coke or an inert such as sand of the Geldart B fluidisation class. The mass ratio of solids to feed oil is 10:1, with rates of bulk solids transport at 0.1 m/s. Fluidisation velocities of 0.6 m/s are used.

The benefits of the cross-flow design can be leveraged in a number of ways. An obvious basis is simply to leverage the capacity benefits introduced as a result of the design, with all other operating parameters kept identical to fluid coking; in this case, the residence time distribution of the solid phase

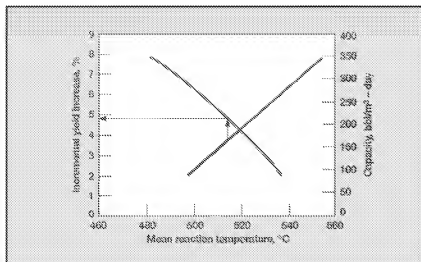


Figure 5 Incremental yield benefit (solid line) associated with the cross-flow coking concept, relative to commercial fluid coking. The capacity of each unit (dotted line) is also shown. Arrows show the incremental yield increase associated with the ETX design, if designed to the same capacity as a commercial fluid coker

Impact of temperature on chemical changes in liquid phase during coking

Temperature, °C	Yield of product oil, %wt	Hydrogen retention in product oil, %
470	74	82
500	72	78
530	68	73

Hydrogen retention is quoted as a percentage of the hydrogen contained in the feed.

Table 1

reduces the reactor size by 65%, when the feedboard, feed and exit zones of the cross-flow unit are considered. Product losses are minimised in two ways: the shallow bed reduces losses to over-cracking by an absolute 2%, and the solids residence time virtually eliminates any short-circuiting of unreacted feed.

A more significant gain can be realised if the operational levers are leveraged to run at lower temperatures. A reduction in temperature is known to manifest itself through a reduction in over-cracking of the liquid products that evolve in the gas phase. The impact of temperature on over-cracking has been well studied (Figure 4). Potential benefits associated with a reduction in temperature as they affect the many reactions in the liquid phase have not appeared in the public domain. To assess the impact of temperature on the liquid phase, a series of rapid heat-up experiments were carried out: using Athabasca vacuum residue as a feedstock, batch experiments were performed in an open quartz reactor purged continuously with nitrogen. Heat was provided by a molten salt bath. The experiments were carried out so that the extent of the reactions in the gas phase were

insignificant, and the results reflected only the processes occurring in the liquid phase. The results were quite surprising: as the reaction temperature was decreased from 530–470°C, the liquid yield increased by 5%, accompanied by an increase in product quality. From a hydrogen balance, almost 10% more of the hydrogen in the feed was retained in the liquid products (Table 1).

Of course, to accommodate the reduced temperatures, additional residence time and solids inventory must be provided in the reactor design. In the cross-flow reactor, these design changes represent a compromise with respect to throughput capacity over the base case, but they do not affect the gas phase residence times, since the bed height remains unaffected. Making the reactor wider can accommodate additional solids throughput. In contrast, the conventional fluid coking reactor would have to be made taller in order to provide the required incremental residence time and solids throughput. This would increase the gas phase residence time and diminish the impact of reduced operating temperatures.

Combining all effects, a reduction in reactor operating temperature to 470°C

would increase liquid yields by 9% over commercial fluid coking. This increase in liquid yield would also be accompanied by a rise in liquid product quality. As discussed, this case would be accompanied by a significant reduction in throughput capacity. At a capacity equal to fluid coking, the average operating temperature of the reactor could be reduced to 515°C, providing a yield benefit of 4% (Figure 5).

Primary upgrading technologies

A number of primary upgrading technologies are competing for the anticipated new barrels of residues coming onto the marketplace. These technologies can be divided into two main camps: hydrogen addition and hydrogen shuffling. The hydrogen addition processes add elemental hydrogen catalytically to the residua, while the hydrogen shuffling process redistributes the hydrogen in the feedstock, producing a product with increased hydrogen content at the expense of a hydrogen-deficient by-product.

There are many variations in process flow sheets centred on these two approaches that incorporate separations based on boiling point or solubility. In fact, processes can be envisioned that are based solely on separation strategies and do not include any chemical conversion step. These strategies do not seem feasible when it is considered that the asphaltene fraction and a portion of the resins are not of acceptable quality to a conventional FCC unit. Where no chemical conversion step is included, this material cannot be processed further. Due to the large volume of feedstock this fraction represents, utilising it solely for its energy equivalence will rarely, if ever, be the most economic option. As a result, this fraction must be upgraded to some extent.

A key question to consider is the appropriate level of conversion. High-conversion hydrogen-addition processes have been developed that can convert almost the entire heaviest fraction in the feedstock. In contrast, hydrogen shuffling cannot ever achieve complete conversion, since a hydrogen-deficient by-product is a requisite, with the maximum theoretical yield being 85% by weight. So how do we decide on a sound level of conversion? Ironically, the answer lies in our increased understanding of coking chemistry. In a hydrogen-addition process, as the feedstock reacts, the species stabilising the heavy aromatic asphaltene molecules are removed as reaction products. At some conversion levels, say 70%, the solubility limit of the

asphaltenes is exceeded and a separate, asphaltene-rich phase is formed; this new phase can then form coke. A solution to this limit is to separate the asphaltenes before the critical reaction extent is exceeded, so that they can be recycled and diluted with fresh feed. In this manner, essentially 100% of the asphaltenes can be converted to product. But at what price? As the conversion is increased, the asphaltenes are more condensed and of a higher boiling point. The mechanism required to achieve high conversion involves catalytic hydrogenation followed by thermal cracking of the newly hydrogenated bonds until the resulting molecules are of sufficient quality to be included with the products. As a result, the gas make associated with incremental product yield is very large, and this gas contains much of the incremental hydrogen added. Capital costs, catalyst and natural gas prices all need to be low to support such a scheme where conversion approaches 100%. When environmental initiatives are considered, the situation is even less attractive, since the carbon dioxide yield associated with incremental production is large at high conversion.

In the current economic environment, coking technologies emerge as attractive options. Of the commercial options, delayed coking possesses a quality

advantage, while fluid coking has an edge with regards to liquid yield. What is desired is a coking technology that has both attributes, such as the ETX design.

Moving forward

Development of a low severity coking process based on current research has been identified as being on the steep part of the development "S" curve. However, the ETX solution, designed to take advantage of these new concepts, is based upon the merger of two mature technologies: cross-flow fluidisation and coking on a fluid bed. The design parameters are all within the commercial design window advertised by vendors of cross-flow technology. This includes operating temperatures and solids fluxes. Coking on fluid beds has been demonstrated for hundreds of operating years. As a result, the ETX design can rely on the many studies and operational data available in the public domain. To advance the cross-flow design, a piloting exercise is seen as necessary, not to prove the concept but rather to prove operability. Small-scale laboratory exercises would only serve to confirm the principles of reactor design that appear in all undergraduate textbooks and would offer no value in the development process.

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Gerard Monaghan is the CEO of Envision Technologies Corp. He is responsible for most of the business aspects of the company and has laid out the economic business case associated with the ETX design. Monaghan holds a bachelors degree in chemistry from the University of Lethbridge, AB, Canada, a bachelors degree in chemical engineering, and a masters degree in business administration, both from the University of Alberta, Edmonton, AB, Canada. Email: monaghan@envisiontech.ab.ca
